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MASS SPECTROMETRIC DETERMINATION  
OF THE COMPOSITION OF THE VENUS CLOUDS

Contract NAS5-23099

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For the design of instruments to analyse the composition of the clouds on the planet Venus, it is necessary to know the results from the Venera and the Mariner probes and also from ground observations. The extensive literature about this subject has been collected and studied. It became apparent that the increased number of data, obtained by various different methods, don't agree to each other. This situation did promote a large number of speculative papers about this subject. It also shows the necessity of a probe especially designed for the analysis of the clouds to remove the discrepancies. A review article about this subject has been recently published by Donald G. Rea.\* He describes two cloud layers. The upper layer has a top altitude of 81 km, where the temperature and the pressure are, respectively, 175° K and 3 mb. The upper cloud layer is optically thin and consists most likely of water in which a small amount of HCl is desolved. The relative concentration of HCl to CO<sub>2</sub>, the main constituent of the Venus atmosphere, is estimated to be  $6 \times 10^{-7}$ . This is beyond the detection limit of normal mass spectrometers.

Two approaches are feasible to obtain this high sensitivity. The first one, consists of a tandom mass-spectrometer which suppresses sufficiently the background from scattered ions to permit detection of impurities in such low concentrations. The instrument itself can be either a magnetic analyzer or a quadrupole or monopole analyzer. The other approach uses an enrichment of the cloud materials compared to the ambient atmosphere, before the sample introduction into the mass spectrometer. This can be performed with different precipitation methods. The

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\* Donald G. Rea, Composition of the Upper Clouds of Venus. Rev. Geo and Space Physics, Vol. 10, 363, 1972.

objective is the production of a liquid which consists only of the cloud particles. There are different possibilities for such an enrichment which will be studied and compared to each other in the near future.

The simplest way to analyse the clouds is to introduce the atmosphere with cloud particles through a molecular leak into the mass spectrometer. This method would result, first of all, in a more accurate determination of the composition of the Venus atmosphere. For instance,  $H_2$  and the rare gases may be present there and included into the nitrogen determination by the Venera probes. If the cloud droplets consist mainly of water with a small amount of HCl or HF, then it can be expected that the droplets will evaporate as soon as pressure is sufficiently low. It is not expected that these droplets would block the capillary. The analysis can be performed in a regular Nier type ion source. However, special care must be taken to use electrode materials which are completely free of Cl and F. The customary procedure to clean the electrodes by washing them in HCl should not be used. As soon as HCl and F are bound to the surface they are very hard to remove, and produce ions if the electron beam hits the surface of the electrodes. With sufficient precautions, it should be possible to reduce the background of HCl from the electrodes below the  $10^{-7}$  level. It is further necessary to use for the capillary and for the electrodes materials which are not attacked by HCl or F.

If a very dilute solution of HCl has to be analyzed, it is necessary that the liquid phase passes through the capillary leak. In this case, the evaporation of the sample occurs at the high vacuum end of the

capillary. This has also the advantage that the ambient  $\text{CO}_2$  of the Venus atmosphere is suppressed. Evaporation of the sample before introduction into the capillary leak is not recommended because, in this case, mainly water would be evaporated first and the  $\text{HCl}$  would remain in the liquid phase until a larger concentration of  $\text{HCl}$  in the liquid phase has been attained. This procedure would therefore suppress the detection of  $\text{HCl}$ .

The controversy whether there are ice crystals in the upper layer of the clouds has not been resolved yet. In conclusion of all the experiments made so far, it is highly unlikely that ice particles exist in an appreciable amount. The distinction between ice particles and liquid droplets has to be done by other methods than the mass spectrometer. If a slightly heated precipitator is used to enrich the cloud particles it will collect the liquid and solid phase simultaneously.

Below this thin cloud layer is the optically dense cloud layer, with the top altitude at 61 km where the temperature is  $260^\circ\text{K}$  and the pressure 240 mb. The available data seem to indicate that the clouds must be composed of a compound formed by a reaction of  $\text{H}_2\text{O}$  with some other compound and having an equilibrium partial pressure of  $\text{H}_2\text{O}$  at  $260^\circ\text{K}$  which is at least two orders of magnitude lower than the partial pressure of ice. Many materials have been suggested; however, the evidence in support of these is very weak or non-existent.

The conductivity gage on the Venera probes showed that the maximum humidity is located in a layer of approximately 10 km thickness and

decreases rapidly at higher and lower levels. The Venera 7 probe has passed the whole cloud layer in approximately 2 minutes. The Venera probes were attached to a parachute which descended with a speed of about 100 meters per second at high altitudes where the clouds are located, down to about 20 meters per second near ground level. This speed is too fast for the direct analysis of the very thin cloud material and also for the collection of a sufficient quantity of liquid for an analysis as described before. The descend velocity can be sufficiently reduced either with a larger parachute or with an additional balloon. More accurate estimates about the necessary sampling time will be made later.

Since the composition of the clouds is completely unknown, the approach to the instrumentation should be such that any material can be detected. A precipitator shall be used to enrich the cloud material in comparison to the ambient atmosphere. The condensed liquid shall be introduced through a capillary to Nier type ion source. Above the cloud layer, only the ambient atmosphere will be introduced through the capillary and analyzed in the mass spectrometer. After the precipitator has collected enough cloud material the liquid will pass through the capillary. This should provide a good spectrum if the clouds consist of water droplets in which a small amount of HCl or HF is dissolved. However, if the water droplets contain an appreciable amount of a salt, for instance  $\text{Fe Cl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{HgI}_2$ , then it is likely that the capillary will be blocked by crystals. In this case, the sample must be introduced into the ion

source through a vacuum lock. After this sample has been put into the ion source, it must be evaporated either in a Knudsen cell or by a laser beam. It will be difficult to install a vacuum lock on a planetary probe, because of the very limited pumping capabilities. As an alternative, introduction of the fog particles through a hydrogen type gas chromatograph should be investigated. Since here the capillary can be considerably wider, because of the pumping hydrogen gas, it is likely that the particles can pass, without blocking, the capillary. This possibility will be more closely investigated in the near future.